PREDICTING LIQUID DENSITIES OF ORGANIC COMPOUNDS
II: NITROGEN AND SULFUR COMPOUNDS

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Abstract

Correlations of liquid densities have been extended to more classes of organic compounds. The products of liquid density and molecular weight at or near 20 °C were previously found to be linear functions of the number and types of carbon atoms in the molecule. Cyclic carbon atoms contributed more to density than carbon atoms not part of a ring structure. Carbon atoms which occupy two rings have since been found to contribute even different increments. Additional databases of liquid densities have been set up for compounds with cyclic oxygen atoms, cyclic and noncyclic nitrogen atoms, and cyclic and noncyclic sulfur atoms. Correlation parameters have been obtained by fitting these data by least squares minimization.

I. Introduction

Liquid densities of many organic compounds are available in original publications and in a few extensive tabulations. However, there are many compounds for which densities are not readily found. Furthermore, there is no easy way to check the accuracies of reported liquid densities. Computer calculations of other properties and processes that require densities as input would be simplified by having a mathematical expression to estimate them. The correlations reported in this and a previous paper[1] have been developed to meet these needs.

The primary source of liquid density data was the CRC Handbook of Chemistry and Physics.[2] Other tabulations and original sources were consulted when a suspicious value was found in the Handbook. At least initially, only liquid densities near normal ambient temperatures have been of concern. Therefore, only density values within the 15-25 °C range of compounds with melting points below 20 °C were used.

II. Review

In the previous paper of this series,[1] it was shown that plots of liquid densities multiplied by molecular weights (LDxMW) vs. number of carbon atoms (c) of the same type were linear. Hydrocarbons fell on the same plots, independent of 1) the number of hydrogen atoms, 2) the type of carbon-carbon bonds, and 3) branching. Both aromatic and alicyclic hydrocarbons coincided on one such plot. However, these cyclic carbon atoms contributed different increments to LDxMW than the noncyclic. Correlations were obtained by linear least squares fitting of 105 data to the equation given below. The resulting parameters and standard deviations of these data are repeated in Table 1.

TABLE 1.

Liquid Density Coefficients for Hydrocarbons

Atom Type (X)	Number of Compounds	Coefficients			Standard Deviation (g/mL)
		k_1	k_2	k_0	
Carbon					
Aliphatic					
Noncyclic (c)		11.639	--	12.104	0.017
Alicyclic/	105 (including both types and mixed)				
Aromatic (cc)		13.803	--	17.128	0.017
Fused					
Bicyclic (ccc)	14	25.107	--	87.410	0.018
Oxygen					
Noncyclic	172	21.523	1.486	3.658	0.052
Cyclic	28	19.167	0.489	-17.425	0.030
Fluorine	20	54.307	-0.540	185.244	0.042
Chlorine	118	51.485	3.240	27.393	0.050
Bromine	55	82.727	34.719	-140.394	0.096
Iodine	30	128.329	105.254	-171.674	0.111
Nitrogen					
Noncyclic	128	22.710	0.212	24.384	0.043
Cyclic	75	18.634	0.875	-5.840	0.032
Sulfur					
Noncyclic	55	34.453	4.243	-2.914	0.029
Cyclic	19	39.780	4.909	-8.442	0.013
Total:	819			Overall:	0.050

Halogenated and oxygenated hydrocarbons also produced linear plots of LDxMW vs. c. Each additional heavy atom of the same type contributed more to LDxMW, so a quadratic term was included in the correlations for these atoms. A small number of points in the databases were recently found to lie outside the selected temperature range. Revised parameters and standard deviations of the data are listed in Table 1.

The correlation coefficients given in Table 1 were obtained by fitting this equation using a nonlinear curve fitting program (SYSTAT from SYSTAT, Inc., Evanston, IL) on an IBM-PC compatible desktop computer. The standard deviations of the data from these fits are also given in Table 1.

III. Fused Bicyclic Hydrocarbons

When naphthalenes and quinolines were included in databases with monocyclic hydrocarbons, biases in the data fits were noticed. These biases were eliminated by treating carbon atoms that were part of both ring structures as different from those that were part of only one. A database of 14 substituted liquid naphthalenes was used to calculate the LDxMW increments of these fused bicyclic carbon atoms (see Table 1). Spiropentane (with one fused bicyclic carbon atom) and indene (with two in fused benzene and cyclopentene rings), two compounds not in the database, were used to confirm this approach:

TABLE 2

Density	Spiropentane	Indene
Experimental:	0.7266	0.9960
Calculated:	0.7213	0.9822
Calculated with all ring carbons treated alike:	0.7617	0.9220

The correlation equation used previously[1] was, therefore, expanded to include the number of this third type of carbon atom (ccc), as well as of noncyclic carbon atoms (c), cyclic carbon atoms (cc), and a type of atom (x) other than carbon and hydrogen, if present:

$$Liquid\ Density = [11.639*c + 13.803*cc + 25.107*ccc$$
$$(g/mL) \quad + k_1*x + k_2*x^2$$
$$-(12.104*c + 17.128*cc + 87.410*ccc$$
$$+ k_0*x)/(c + cc + ccc + x)]/MW$$

The coefficients 25.107 and 87.410 are the correlation values obtained by fitting this equation to the bicyclic fused hydrocarbons database. The k_i's are similar coefficients for other atoms and their positions in a molecule (discussed below).

IV. Cyclic Oxygens

Compounds with oxygen atoms as part of their ring structure were not considered in the previous work. A database of liquid densities of 28 such compounds has been established and fit to the model. Cyclic, fused bicyclic, and noncyclic carbon atoms were included, but only one type of oxygen atom (in a ring). There were 12 furans, 2 pyrans, 5 benzofurans, and 9 dioxanes. Table 1 shows the correlation parameters obtained with a standard deviation of 0.030 g/mL. Figure 1 shows a comparison between calculated and experimental densities for these 28 compounds.
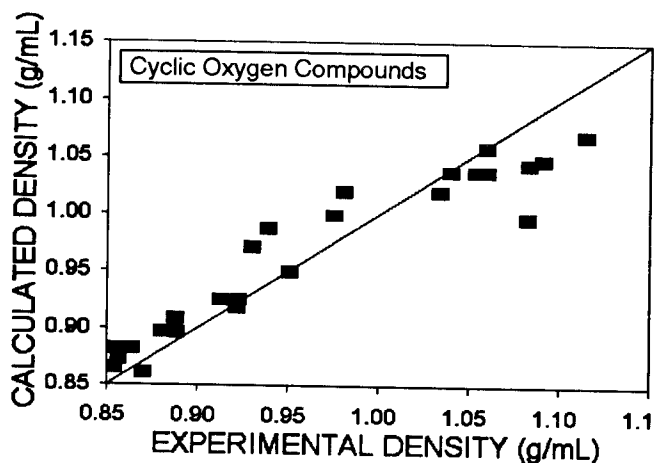
Figure 1.

V. Nitrogens

The database of 128 compounds containing noncyclic nitrogen atoms included amines, imines, hydrazines, nitriles, isocyanates, and anilines. The coefficients and standard deviation obtained by fitting these points to the above equation are listed in Table 1.
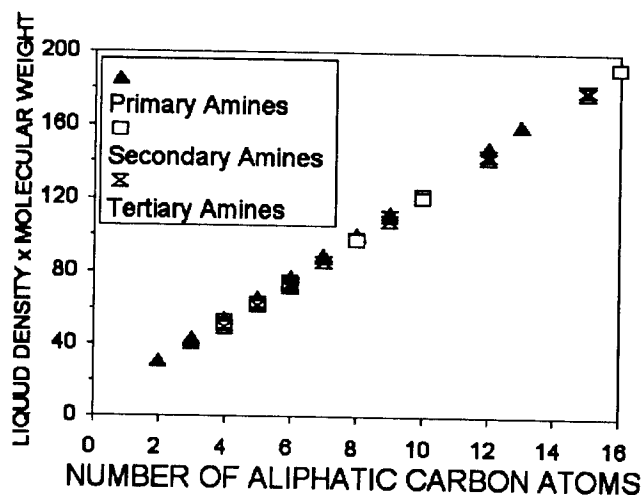

Figure 2.

Figure 2 shows the LDxMW vs. c plot for aliphatic monoamines. Densities of primary, secondary, and tertiary amines were indistinguishable.
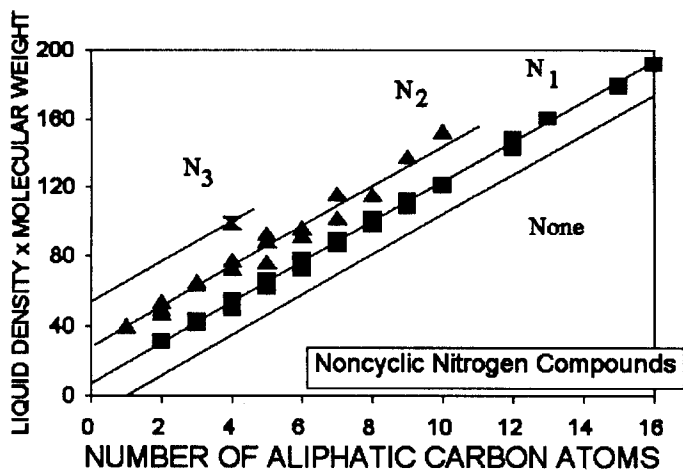

Figure 3.

Figure 3 shows the effect of added noncyclic nitrogen atoms. The slope remains the same, but the intercept is shifted for each added nitrogen. This is what was observed with oxygen and halogen atoms.
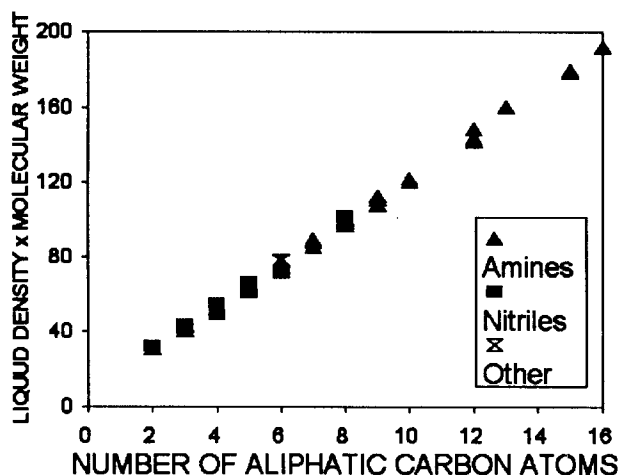

Figure 4.

Figure 4 shows a LDxMW plot for amines, nitriles, and other compounds without nitrogen atoms in a ring structure. These points are all essentially coincident, demonstrating once again, as with oxygen compounds, the absence of significant hydrogen bonding and polarity effects on liquid densities. Hydrogen bonding and polarity are much greater in amines and hydrazines than in the other nitrogen compounds.
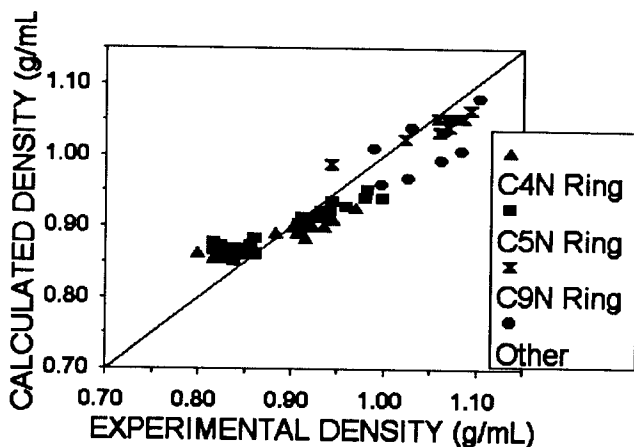
Figure 5.

Another database included 75 compounds with nitrogen as part of a hydrocarbon ring (cyclic nitrogen atoms): pyrroles and pyrrolidines (C_4N); pyridines and piperidines (C_5N); pyrazines (C_4N_2); quinolines and isoquinolines (C_9N). Figure 5 shows how well liquid densities of these nitrogenated hydrocarbons were fit by the coefficients given in Table 1.

VI. Sulfurs

The database of sulfonated hydrocarbons contained 55 compounds with noncyclic sulfurs, mostly mono- and polysulfides and mono- and polythiols. It also contained 19 compounds with 1-2 sulfur atoms and 2-6 carbon atoms in ring structures. The coefficients obtained from fitting the model separately to these two types of sulfur atoms are given in Table 1. Figure 6 shows a comparison of densities calculated using these coefficients with densities reported.[2]
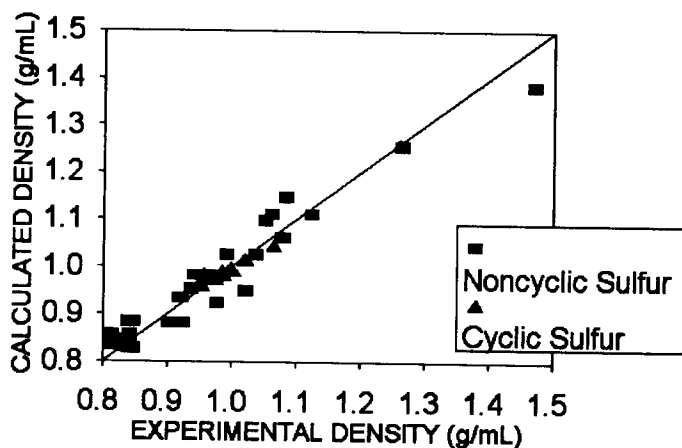

Figure 6.

CONCLUSIONS

Correlations have been developed for liquid densities near 20 °C of oxygen-, sulfur-, and nitrogen-containing hydrocarbons. These supplement the correlations obtained for hydrocarbons and halocarbons, including straight chain, branched chain, alicyclic, aromatic, and polycyclic. The overall standard deviation of calculated liquid densities of 819 compounds from reported values was 0.05 g/mL. The accuracy for compounds containing only carbon and hydrogen was one-third of this. With nitrogen-containing hydrocarbons, no effects of type of amine, polarity, or hydrogen bonding on liquid densities were apparent.

These correlations provide ways of checking reported densities and calculating densities not reported. The only inputs needed for estimating liquid densities near 20 °C are atom composition and molecular structure.

REFERENCES

1. Wood, G. O., and T. B. Weaver, "Predicting Liquid Densities of Organic Compounds I. Halogenated and Oxygenated," in _Proceedings of the 1991 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research, November 1991_, Aberdeen Proving Ground, MD, 1991.

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